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Correlation Times and Complex Polarisability for Linear and Spherical Top Molecules

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Abstract: We describe a simple method for calculating correlation times and complex polarisabilities from the orientational autocorrelation functions of molecules executing rotational Brownian motion. The expression for the autocorrelation function is first rearranged to display explicitly its asymptotic form for large times. We apply the method to recent results on the autocorrelation functions for linear and spherical-top molecules.

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Calculations [1, 2, 3] of the normalized orientational autocorrelation functions $\Phi(t)$ of linear and spherical-top molecules yield expressions of the form

$$\Phi(t) = \exp\{\int_0^t S(s)\,ds\}\ , \tag{1}$$

where

$$S(t) = \gamma S_1(t) + \gamma^2 S_2(t) + \cdots \tag{2}$$

with $\gamma = kT/IB^2$; I is the moment of inertia and B^{-1} is the frictional relaxation time. The form (1) is inconvenient as it stands for the computation [4] of quantities such as the complex polarisation and the correlation times. It is the purpose of this note to show how by a simple rearrangement of the expression (2) one can readily obtain these quantities, and to give explicit expressions for them. The point is that one must calculate integrals of the form

$$\int_0^\infty \exp\{\int_0^t S(s)ds\}\, e^{i\omega t}\,dt \tag{3}$$

which are intractable as they stand; using the power series for the exponential function does not help matters as $\int_0^t S(s)\,ds$ increases linearly as t increases. Instead we use the identity

$$\int_0^t S(s)\,ds = S(\infty)t + \int_0^\infty \{S(s) - S(\infty)\}\,ds - \int_t^\infty \{S(s) - S(\infty)\}\,ds \tag{4}$$

to write (2) as

$$\Phi(t) = A\, e^{-Gt} F(t), \tag{5}$$

where

$$A = \exp\left[\int_0^\infty \{S(s) - S(\infty)\}\, ds\right], \tag{6}$$

$$G = -S(\infty) = -\gamma S_1(\infty) - \gamma^2 S_2(\infty) - \cdots, \tag{7}$$

$$F(t) = \exp\left[-\int_t^\infty \{S(s) - S(\infty)\}\, ds\right]. \tag{8}$$

The exponent in (8) is bounded for all $t \geq 0$ in the problems we are considering, and the series expansion of $F(t)$ in powers of γ can now be integrated term-by-term. We put

$$F(t) = 1 + \gamma F_1(t) + \gamma^2 F_2(t) + \cdots, \tag{9}$$

where

$$F_1(t) = -\int_t^\infty \{S_1(s) - S_1(\infty)\}\, ds, \tag{10}$$

$$F_2(t) = \tfrac{1}{2}\left[\int_t^\infty \{S_1(s) - S_1(\infty)\}\, ds\right]^2 - \int_t^\infty \{S_2(s) - S_2(\infty)\}\, ds, \tag{11}$$

and so on. By using (9), the integrals (3) can be carried out straightforwardly.

The complex polarisability $\alpha(\omega)$ is given by

$$\alpha(\omega) = (\mu^2/3kT)\left[1 - i\omega \int_0^\infty e^{-i\omega t}\, \Phi_0^1(t)\, dt\right], \tag{12}$$

where μ is the electrical dipole moment. The correlation times τ_j are given by

$$\tau_j = \int_0^\infty \Phi_0^j(t)\, dt. \tag{13}$$

Here Φ_m^j is the autocorrelation function of the spherical harmonic Y_{jm}:

$$\Phi_m^j(t) = \int_0^\pi \int_0^{2\pi} \langle Y_{jm}(\theta(t), \varphi(t))^* Y_{jm}(\theta, \varphi) \rangle \sin\theta\, d\theta\, d\varphi. \tag{14}$$

For spherical-top molecules the Φ_m^j are independent of m; for linear molecules they depend on m, but only the $m = 0$ functions are of physical interest. In the papers [1, 2, 3] the after-effect functions $\langle D^j_{mm'}(\alpha(t), \beta(t), \gamma(t)) \rangle$ are calculated. Here the $D^j_{mm'}$ are the matrix elements of the rotation matrices in the $(2j+1)$-dimensional irreducible representation of the rotation group (as given in [6], for example). The after-effect functions are formally identical with the correlation functions; for spherical-top molecules we have

$$\langle D^j_{mm'}(\alpha(t), \beta(t), \gamma(t)) \rangle = \delta_{mm'}\, \Phi_m^j(t). \tag{15}$$

Next we apply these ideas to the expressions for $S(t)$ for spherical-top molecules given in [1, 2]. After a considerable amount of tedious but elementary manipulation we obtain:

$$G_j = j(j+1)B\left\{\gamma + \tfrac{1}{2}\gamma^2 + \tfrac{7}{12}\gamma^3 + \left[\tfrac{17}{18} - \tfrac{1}{8}j(j+1)\right]\gamma^4 + \cdots\right\}, \tag{16}$$

$$\tau_j = \{j(j+1)B\gamma\}^{-1}\left\{1 + \left[j(j+1) - \tfrac{1}{2}\right]\gamma + \left[-\tfrac{1}{3} + \tfrac{3}{4}j(j+1) - \tfrac{1}{2}j^2(j+1)^2\right]\gamma^2 + \left[-\tfrac{55}{72} + \tfrac{23}{18}j(j+1) - \tfrac{9}{8}j^2(j+1)^2 + \tfrac{5}{12}j^3(j+1)^3\right]\gamma^3 + \cdots\right\}, \tag{17}$$

$$\alpha(\omega)/\alpha(0) = \frac{G_1(G_1+B)}{(G_1+i\omega)(G_1+B+i\omega)} - \frac{i\omega G_1^2\left\{\frac{5}{2}(G_1+i\omega) + \frac{7}{2}B\right\}}{(G_1+i\omega)(G_1+B+i\omega)^2(G_1+2B+i\omega)} \tag{18}$$

$$- \frac{i\omega G_1^3\left\{(G_1+i\omega)^4 + 93(G_1+i\omega)^3 B + 175(G_1+i\omega)^2 B^2 + 783(G_1+i\omega)B^3 + 424B^4\right\}}{48B(G_1+i\omega)(G_1+B+i\omega)^3(G_1+2B+i\omega)^2(G_1+3B+i\omega)} + \cdots$$

In the expression for $\alpha(\omega)$ we have used (16) to eliminate γ in favour of G_1. The first term on the right hand side of (18) is of the same form as the well-known Rocard empirical expression [5]; the second and third terms are of order γ^2 and γ^3 relative to the first.

The calculation of $S(t)$ to a given order in γ involves considerably more labour for a linear molecule than for a spherical-top molecule. In [3] the calculations of $S(t)$ for a linear molecule was carried through to order γ^3; from these results we have

$$G_j = j(j+1)B\{\gamma + \gamma^2 + \tfrac{8}{3}\gamma^3 + \cdots\}, \qquad (19)$$

$$\tau_j = \{j(j+1)\gamma B\}^{-1}\{1 + [j(j+1)-1]\gamma + [-\tfrac{5}{3} + \tfrac{3}{2}j(j+1) - \tfrac{1}{2}j^2(j+1)^2]\gamma^2 + \cdots\}, \qquad (20)$$

$$\alpha(\omega)/\alpha(0) = \frac{G_1(G_1+B)}{(G_1+i\omega)(G_1+B+i\omega)} - \frac{i\omega G_1^2\{\frac{3}{2}(G_1+i\omega)+\frac{5}{2}B\}}{(G_1+i\omega)(G_1+B+i\omega)^2(G_1+2B+i\omega)} + \cdots \qquad (21)$$

Many authors (see for example [5]) have pointed out that the leading terms in the expression for $\alpha(\omega)$ can be cast in the Rocard form. However, it does not seem to have been noticed that, by eliminating γ in favour of G_1, the first correction can be made of relative order γ^2, rather than of order γ.

It is of interest to compare the expression (5) for the autocorrelation function with the classical theory of Debye which neglects inertial effects, corresponding to setting $A=1$, $G=2\gamma B$, $F(t)=1$ in (5). The theory used to derive expressions of the form (1) uses a stochastic representation of the medium surrounding the molecule. The state of the surrounding medium (the heat bath) is described by a single parameter, the temperature T; the interaction of the molecule with the heat bath is also described by a single parameter, the rotational drag coefficient IB. Two relaxation times appear in the theory: IB/kT and B^{-1}; the theory is valid when their ratio $\gamma = kT/IB^2$ is small. The autocorrelation functions fall off exponentially on the scale of IB/kT, and the short-time correction factor $F(t)$ tends to unity on the scale of B^{-1}. Thus the inertial corrections to the Debye theory enter in two ways:

(1) There is a modified short-time behaviour described by $F(t)$.

(2) The long-time behaviour is still exponential but with a modified Debye time G^{-1} and a modified normalization A.

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